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LOW TEMPERATURE FLUORINE CHEMISTRY OF ELECTRONEGATIVE ELEMENTS. (U)

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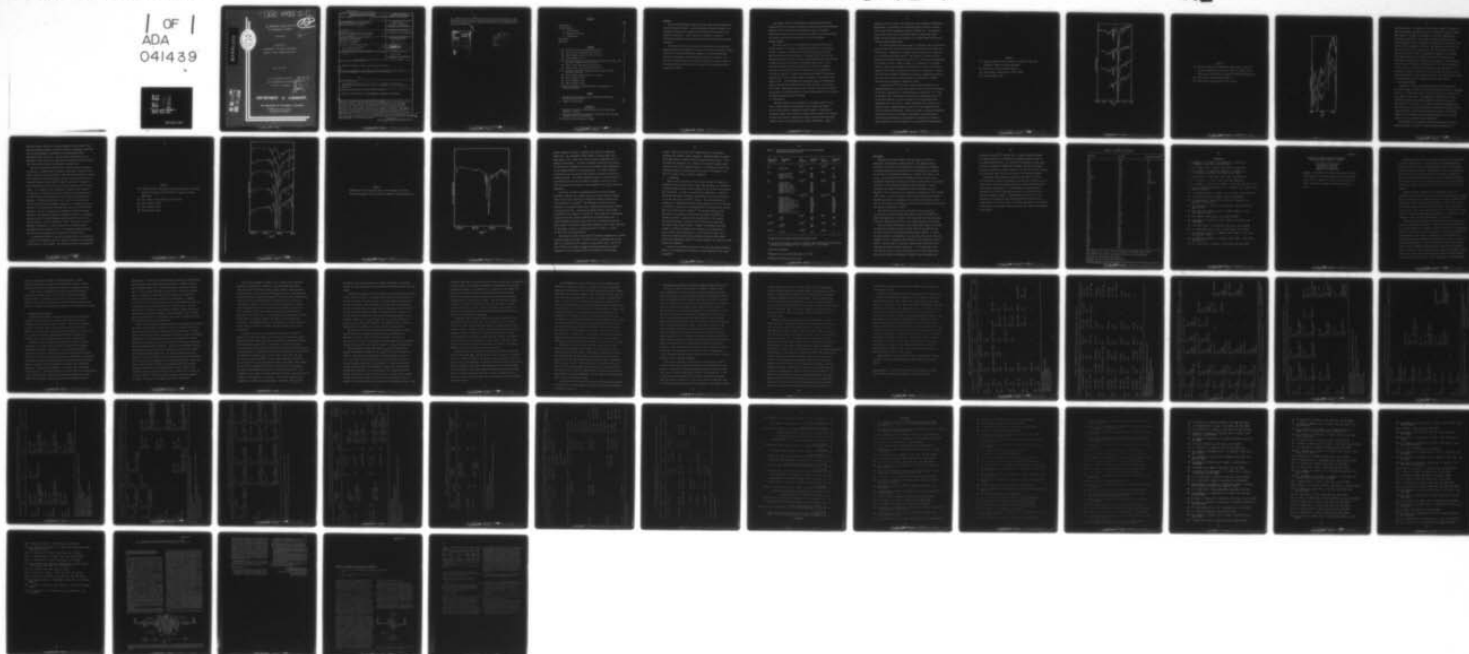
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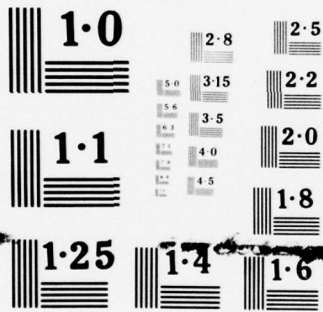
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LOW TEMPERATURE FLUORINE CHEMISTRY
OF ELECTRONEGATIVE ELEMENTS

Final Report

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Abstract

Several new interhalogen species have been prepared and characterized by matrix isolation methods. Bromine difluoride, dibromine fluoride, and dibromine difluoride have tentatively been identified by infrared matrix isolation spectroscopy. These species were formed in a number of different experiments utilizing both UV-photolysis and microwave discharge excitation.

The chlorine and bromine hexafluoride radicals have been prepared by gamma-radiolysis of approximately five mole per cent of the precursor molecule (chlorine or bromine pentafluoride) suspended in a sulfur hexafluoride matrix and subsequently characterized by electron spin resonance. The previously reported chlorine tetrafluoride radical has also been formed by the same technique utilizing chlorine trifluoride or pentafluoride/sulfur hexafluoride mixtures.

This program involved low-temperature synthesis and spectroscopic characterization of new species containing fluorine and other electronegative elements, such as chlorine and other halogens, oxygen and nitrogen. Characterization was carried out by Fourier transform infrared spectroscopy and electron spin resonance using matrix isolation techniques.

Infrared Studies

The major thrust of our low temperature matrix-isolation infrared studies consisted of attempts to prepare and stabilize the radical BrF_2 in order to compare its bonding and structural properties with other known "electron rich" radical species. Presently $\text{ClF}_2^{1,2}$ and Cl_2F^3 are apparently the only 21 valence electron interhalogen radicals that have been at least partially characterized by vibrational spectroscopy. Other 21 electron radicals, including Cl_3^4 and Br_3^5 , which were originally reported to be formed by microwave discharge were in all probability the ionic X_3^- species.⁶ Based on the recent Raman results² and previous infrared data¹, the ClF_2 radical appears to possess an intermediate bond angle of $\sim 150^\circ$. Such bond angles are apparently unique for interhalogen species since the bond angles for most of these molecules are very near 90° or 180° . Experimental data for other "electron rich" radical species, such as BrF_2 , are clearly needed for a better understanding of the structure and bonding prevalent in such molecules.

A. UV-Photolysis

The matrix mixtures were deposited on a CsI window cooled to 14°K with a Cryodyne Model 350 closed-cycle helium refrigerator adapted for use with electronic temperature control equipment. Photolyses of the matrix samples were carried out through a quartz window on the cryostat assembly with radiation emitted from a General Electric Model BH-6 high-pressure mercury arc lamp utilizing two filter combinations. Filter I

consisted of an 11 cm quartz cell filled with water (transmits ~ 200 – 900 nm), while Filter II consisted of the water-filled quartz cell plus a Corning CS-7-54 glass filter (combination transmits ~ 280 – 420 nm). Low-resolution spectra were scanned with a Perkin-Elmer Model 337 spectrometer while higher resolution spectra were obtained with a Digilab Model FTS-20 Fourier Transform infrared spectrometer.

The initial approach involved attempts to synthesize BrF_2 by photodetachment of F atoms from the parent BrF_3 molecule isolated in an Ar matrix via UV-photolysis. UV-photolysis of BrF_3/Ar mixtures results in the appearance of a new infrared band near 570 cm^{-1} . The increase in intensity of this weak feature on thermal cycling from 14° to 25° to 14°K and the disappearance of the band at $\sim 35^\circ\text{K}$, as shown in Figure 1, is indicative of an unstable species. BrF_3/Ar matrix samples were subjected to a variety of photolysis conditions in an effort to optimize the yield of the new species. However, with the current photolysis equipment consisting of a high-pressure mercury arc source and a variety of glass filters, no experimental conditions were found which sufficiently enhanced the yield.

In the ClF_2 work,^{1,2} the poorest radical yields resulted from the photodecomposition of ClF_3 while the greatest yields came from the photolysis of ClF and F_2 codeposited in a matrix through the reaction $\text{ClF} + \text{F} \rightarrow \text{ClF}_2$. An analogous route for production of BrF_2 from the photolysis of $\text{BrF} + \text{F}_2$ is much more difficult to carry out because of the disproportionation equilibrium $3\text{BrF} = \text{Br}_2 + \text{BrF}_3$.⁷ Several experiments were carried out in which the above equilibrium mixture diluted in Ar was codeposited with an F_2/Ar mixture and photolyzed. Efforts were made to maximize the quantity of BrF and at the same time minimize interference from other species. The difficulty encountered by this approach is illustrated in Figure 2A which represents the infrared spectrum of the codeposited $\text{Br}_2, \text{BrF}_3, \text{BrF}/\text{Ar}$

Figure 1.

- (a) Infrared spectrum of BrF_3 isolated in Ar (BrF_3/Ar mole ratio $\sim 1/2000$, 17 mmoles of mixture deposited)
- (b) After 25 min. photolysis with Filter II.
- (c) After thermal cycling (14°K to 25°K to 14°K).
- (d) After warming to 33°K .

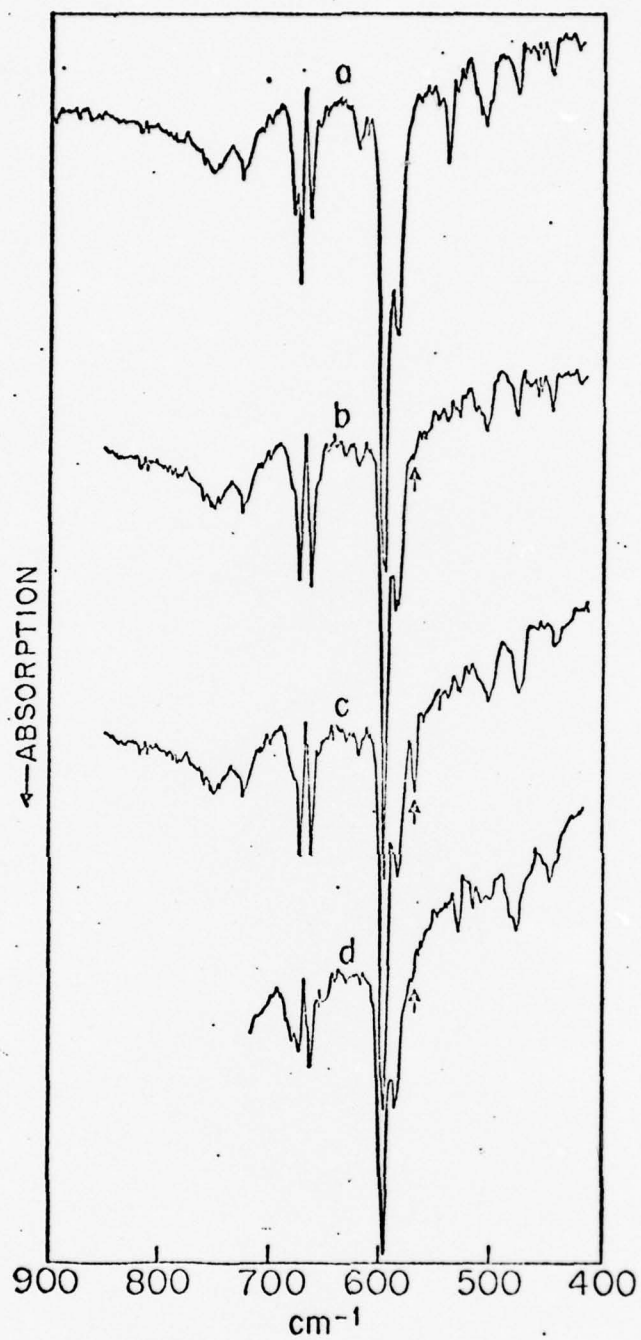
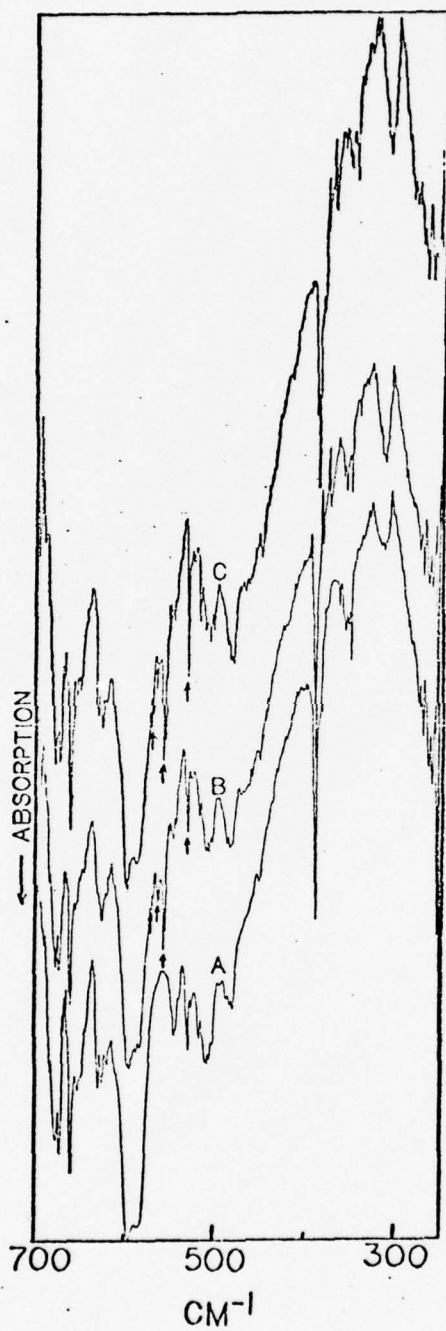


Figure 2.

- (A) Infrared spectrum of an equilibrium mixture of Br_2 , BrF_3 , and BrF in Ar codeposited with F_2 in Ar (Br_2 , BrF_3 , BrF/Ar ratio $\sim 1/50$, F_2/Ar ratio $\sim 1/170$, 8.5 mmoles of each mixture deposited).
- (B) After 40 min. photolysis with Filter II.
- (C) After thermal cycling (14°K to 25°K to 14°K).



and F_2/Ar mixtures. In addition to the BrF band at 660cm^{-1} in Figure 2A, there are numerous other bands which can be attributed to BrF_3 and perhaps other species. Although the complexity of this system appeared to be prohibitive, photolysis of this sample was carried out which resulted in the appearance of three new doublets at $569,567\text{ cm}^{-1}$, $561,563\text{ cm}^{-1}$, and $556,554\text{ cm}^{-1}$ as indicated in Figure 2B. The intensities of 568 cm^{-1} and 555 cm^{-1} bands as well as a band at 527 cm^{-1} were enhanced by thermal cycling (14° to 25° to $14^\circ K$) as illustrated in Figure 2C. The $569,567\text{ cm}^{-1}$ doublet apparently corresponds to the 570 cm^{-1} band previously mentioned in the photolysis of BrF_3/Ar matrix mixtures. The significance of the $556,554\text{ cm}^{-1}$ doublet and the band at 527 cm^{-1} will be discussed in a later section. One interesting side-light to this particular set of experiments involved the observation that the matrix film took on a blue tint after photolysis, which remained even after the sample had been warmed to the temperature where the vaporization of the argon occurs.

B. Microwave Discharge

A Raytheon Microtherm Model CMD-10 microwave diathermy generator was used to supply a maximum of 125 watts of microwave energy at a wavelength of 12.2 cm. The microwave energy is directed by means of a coaxial cable to an Evenson- type cavity. The discharge was initiated in a Lucalox (high-purity alumina) tube after attaining a steady gas flow rate in the range 0.5 to 1.0 cc/min. This system was operated at approximately 80% full power with the variable coupler and tuning screw adjusted so that a maximum forward to reflected power ratio was achieved. Gas mixtures subjected to the discharge were subsequently deposited on a CsI window cooled to $14^\circ K$ for infrared spectral observation.

This approach to the synthesis of BrF_2 was stimulated by a recent report involving the synthesis of BrF by microwave discharge of an

$F_2/Br_2/Ar$ mixture utilized in a mass spectrometric kinetic study.⁸ This particular approach appeared to present a method for producing "purer" BrF which could subsequently be deposited at low temperatures before disproportionation could occur. Also by using an excess amount of F_2 , additional F atoms formed in the discharge and deposited along with the BrF could yield further reaction in the matrix to produce BrF_2 .

The initial experiment utilizing this particular approach consisted of preparing a 1:2:200 mixture of $Br_2/F_2/Ar$ and passing a portion of this mixture through a microwave discharge. This method was complicated, however, by the production of BrF_3 and BrF_5 in addition to BrF as evidenced by the respective infrared bands at 595cm^{-1} , 635cm^{-1} , and 660cm^{-1} in Figure 3A. Three weak features at 527, 507, and 475cm^{-1} in Figure 3A are also worth noting. It is apparent, after examination of Figure 4 which represents the spectrum of a $Br_2/F_2/Ar$ mixture not subjected to the discharge, that the three features just mentioned are due to species resulting from the discharge. On thermal cycling (14° to 25° to 14° K) the intensity of the 527cm^{-1} band increases slightly (Figure 3B). On warming to 30° K the intensity of this band further increases while that of the 507cm^{-1} band diminishes. The 527cm^{-1} appears to correspond to the band previously mentioned in the photolysis experiment exhibited in Figure 2. On further warming the 527cm^{-1} feature disappears indicating that it is due to an unstable species, as is also the 507cm^{-1} band. The feature at 475cm^{-1} apparently corresponds to a stable species as its intensity remains unchanged even after warming to 50° K. The intensity behavior resulting from the various warming cycles is illustrated in Figures 3B-3E.

In determining whether the F_2 and Br_2 reacted prior to the discharge, a portion of the $Br_2/F_2/Ar$ mixture of identical concentration was deposited in the absence of the discharge. The infrared spectrum of this deposited

Figure 3.

- (A) Infrared spectrum of $\text{Br}_2/\text{F}_2/\text{Ar}$ mixture passed through a microwave discharge ($\text{Br}_2/\text{F}_2/\text{Ar}$ ratio $\sim 1/2.5/425$, 10 mmoles of mixture deposited).
- (B) After thermal cycling (14°K to 25°K to 14°K).
- (C) After warming to 30°K .
- (D) After warming to 40°K .
- (E) After warming to 50°K .

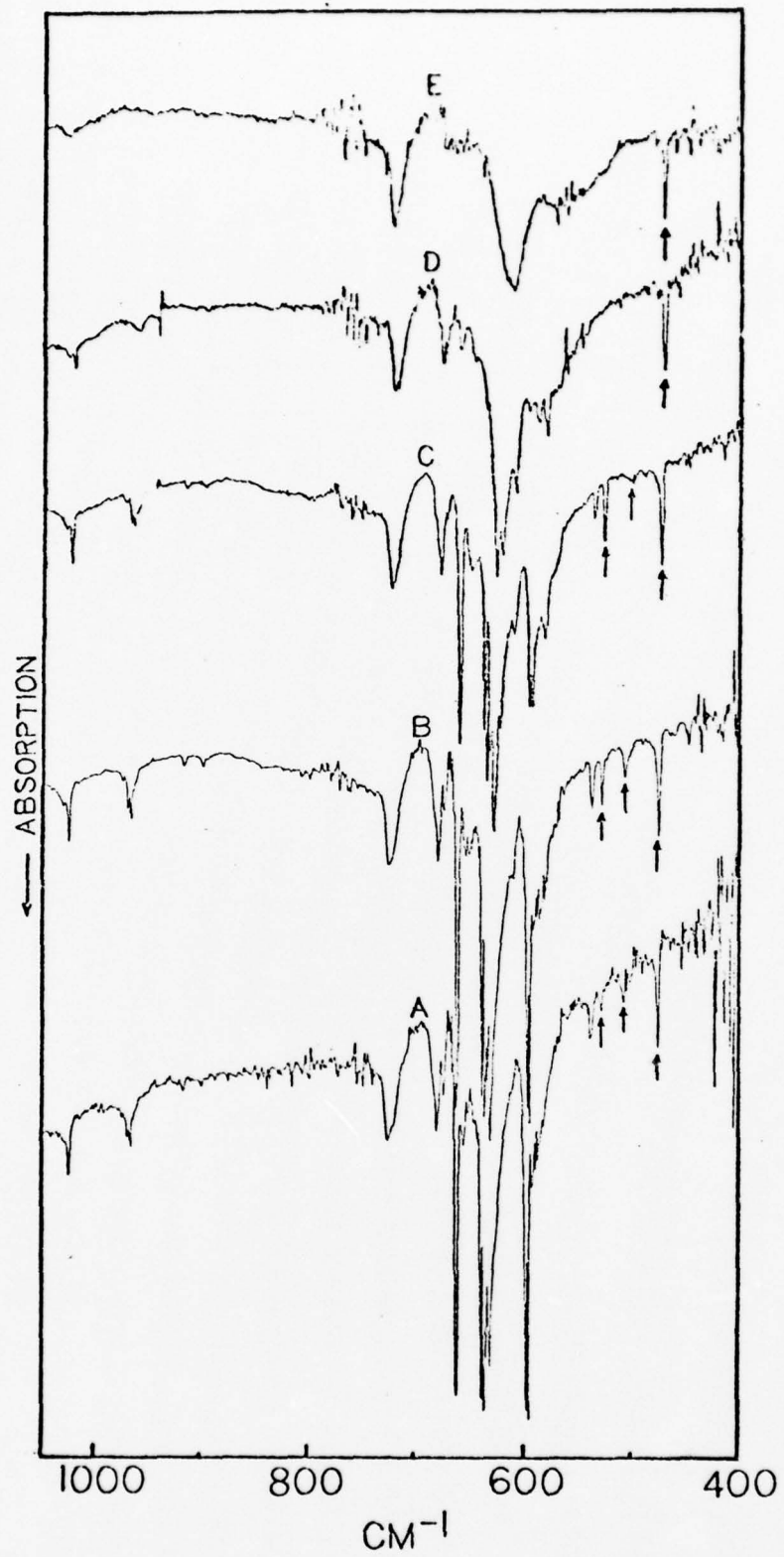
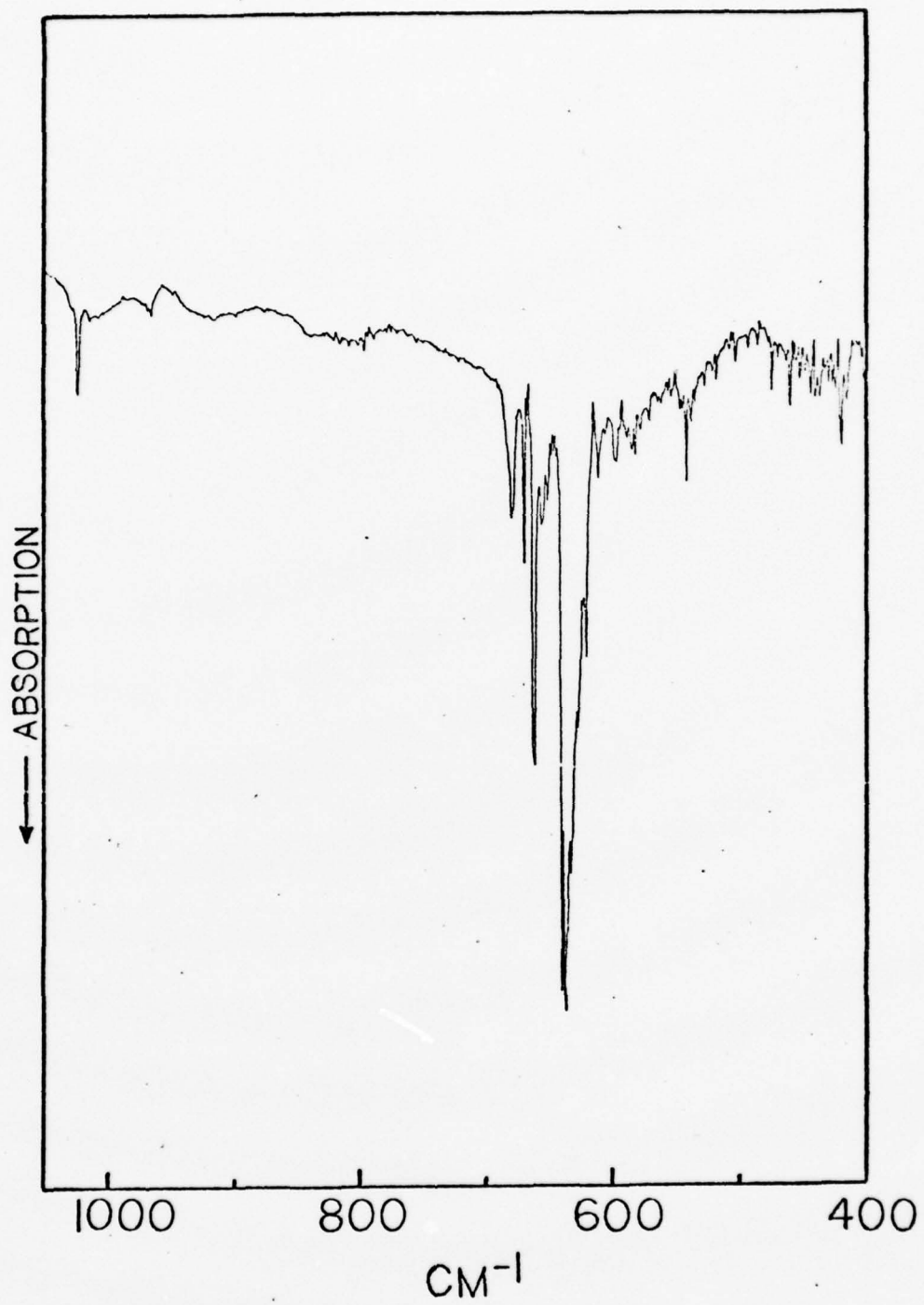


Figure 4.

Infrared spectrum of $\text{Br}_2/\text{F}_2/\text{Ar}$ mixture not subjected to microwave discharge ($\text{Br}_2/\text{F}_2/\text{Ar}$ ratio $\sim 1/2.5/425$, 10 mmoles of mixture deposited).



mixture, depicted in Figure 4, indicates that there is a significant prereaction. The predominant product appears to be BrF_5 along with a minor amount of BrF . Bands due to BrF_3 are absent indicating that it is formed in the discharge. In order to minimize prereaction of F_2 and Br_2 , the experiment was modified so that the two reactants mixed separately in Ar were brought together in the discharge tube. The results obtained utilizing this approach differed only slightly from those involving the premixed reactants. The primary difference appeared in the observation of an additional weak feature near 570cm^{-1} on warming of the matrix film. This band apparently corresponds to that observed in the BrF_3/Ar photolysis experiments.

The results from both the UV-photolysis and microwave discharge experiments indicate that a number of new Br-F species have been formed. Similar results have recently been obtained by Professor Andrews' group at the University of Virginia.⁹ One experiment at Virginia involved deposition of a $\text{Br}_2/\text{F}_2/\text{Ar}$ sample from a common vessel which gives a mixture of Br_2 , F_2 , BrF and BrF_3 . Photolysis and thermal cycling of this sample resulted in two new doublets at $568,570\text{ cm}^{-1}$ and $554,556\text{ cm}^{-1}$ corresponding to bands that we had previously observed in our UV-photolysis work. A second experiment by Andrews' group consisted of codepositing Br_2/Ar and F_2/Ar mixtures from separate vessels which produced no BrF or BrF_3 . Photolysis of this sample produced a very strong $554,556\text{ cm}^{-1}$ doublet, a strong 507 cm^{-1} band, and weak BrF_3 bands.

Based upon our present joint results¹⁰ tentative assignments for a number of the new bands can be made. The 570cm^{-1} band is apparently due to BrF_2 since it is observed only in presence of either BrF or BrF_3 . The 555 and 507 cm^{-1} bands are assigned to Br_2F_2 and Br_2F , respectively, in a manner analogous to that for Cl_2F_2 and Cl_2F in the photolysis of the Cl_2+F_2

system.³ The 527 cm^{-1} and 475 cm^{-1} bands observed in the microwave discharge work presently remain unassigned. Raman experiments by Andrews' group should help to further clarify the bromine-fluorine system. A list of vibrational frequencies for a number of Cl-F and Br-F neutral species is given in Table I for comparison purposes. It should be mentioned that based upon frequency comparisons from this Table, the assignment of the 570 cm^{-1} feature to BrF_2 is somewhat unexpected.

C. γ - Radiolysis

Another area of infrared work has involved attempts to prepare and characterize radical species such as ClF_4 , ClF_6 , and BrF_6 , by γ -radiolysis of matrix mixtures similar to those utilized in the electron spin resonance work (see below). In order to carry out these experiments, a miniature liquid nitrogen-cooled cryostat was constructed of the correct dimensions to fit into the cavity of the ^{60}Co γ -source. The initial experiments consisted of γ -radiolyzing thin films of SF_6 deposited onto a CsI substrate in an effort to make infrared characterization of the SF_5 and SF_6^- radicals known to be formed from esr studies.¹⁵ The infrared spectrum of the SF_5 radical has recently been reported by Smardzewski and Fox¹⁶ and, therefore, provides a good check of the feasibility of this method. The reported SF_5 bands are 812 and 552 cm^{-1} which are in areas where thin films of SF_6 transmit readily. A number of experiments involving a number of different radiolysis times resulted in the observation of no new features in the SF_6 spectrum. It was felt that if SF_5 or SF_6^- could not be characterized by this method that there was little chance of observing interhalogen radicals in 5 mole % mixtures and, therefore, these studies were suspended.

A review of the vibrational spectra of the main group binary fluorides, which is to be submitted for publication, has been included in this report as Appendix I.

Table I. Vibrational Frequencies of Neutral Chlorine-Fluorine and Bromine-Fluorine Species^a

Point Group Symmetry	Vibrational Mode ^b	Cl-F Compound	Frequency (cm ⁻¹)	Br-F Compound	Frequency (cm ⁻¹)
$C_{\infty v}$	$\nu_e (\Sigma^+) - \nu X-F$	$Cl-F^2$	760	$Br-F^{11}$	660
C_{2v}	$\nu_1 (A_1) - \nu X-F$ sym. $\nu_2 (A_1) - \delta F-X-F$ $\nu_3 (B_2) - \nu X-F$ asym.	$ClF_2^{1,2}$	500 242 578	BrF_2	--- --- 570 ^c
C_{2v}	$\nu_1 (A_1) - \nu X-F'$ $\nu_2 (A_1) - \nu X-F$ sym. $\nu_3 (A_1) - \delta F-X-F$ i.p. $\nu_4 (B_1) - \nu X-F$ asym. $\nu_5 (B_1) - \delta F-X-F'$ i.p. $\nu_6 (B_2) - \delta F-X-F$ o.p.	ClF_3^{12}	754 523 328 683 431 332	BrF_3^{12}	672 547 235 597 347 252
C_{4v}	$\nu_1 (A_1) - \nu X-F'$ $\nu_2 (A_1) - \nu X-F$ sym. $\nu_3 (A_1) - \delta F-X-F$ sym.o.p. $\nu_4 (B_1) - \nu X-F$ asym. $\nu_5 (B_1) - \delta F-X-F$ asym.o.p. $\nu_6 (B_2) - \delta F-X-F$ asym.i.p. $\nu_7 (E) - \nu X-F$ asym. $\nu_8 (E) - \delta F-X-F'$ $\nu_9 (E) - \delta F-X-F$ asym.i.p.	$ClF_5^{13,14}$	722 539 493 480 ^d 346 ^e 375 ^d 726 482 299	$BrF_5^{12,14}$	681 582 366 535 ^d 281 ^e 312 ^d 636 415 240
$C_s (?)$	$\nu X-F$ $\nu X-X$	Cl_2F^3	536 302	Br_2F	507 ^c ---
$C_{2v} (?)$	$\nu F-X-F$ $\nu X-X$	$Cl_2F_2^3$	638 462	Br_2F_2	556 ^c
$C_{2v} (?)$	$\nu F-X-F$	$Cl_2F_3^3$	559	Br_2F_3	---

^aFrequencies were obtained from matrix-isolation work.^b ν represents stretching, δ represents bending, unique fluorine atom indicated by F' in XF_3 and XF_5 compounds; i.p. - in plane; o.p. - out-of-plane.^cTentative assignments.^dFrequencies from gas phase Raman work, ref. (14).^eCalculated frequency from ref. (14).

ESR Studies

Electron spin resonance studies were performed in an effort to characterize new fluorine-containing radicals. The approach that was utilized in much of this work (conducted in collaboration with Professor T. Ffrancon Williams and his group), involved γ -irradiation of a mixture of the precursor interhalogen suspended in a suitable solid matrix, such as SF_6 . The procedure consisted of preparing a gaseous mixture of the appropriate interhalogen and matrix gas (optimum concentration of interhalogen ~ 5 mole%) in a well passivated stainless steel vacuum line. A small fraction of the mixture was condensed into either Suprasil quartz or FEP Teflon tubes and sealed off for subsequent γ -radiolysis at 77°K utilizing a ^{60}Co source. The esr spectrum was then recorded using the Varian Model 4502 ESR spectrometer at a temperature that yields good isotropic spectra while at the same time maintaining radical lifetimes sufficient for observation (for SF_6 this temperature is $\sim 105^\circ\text{K}$).

This approach has proven to be successful in the preparation of the previously unreported interhalogen radicals, ClF_6^{17} and BrF_6^{18} (For details see Appendices II and III). The ClF_4 radical which was previously reported by Preston and Morton¹⁹ is also readily prepared by this method.

The net reaction by which most of the interhalogen radicals are formed utilizing this technique appears to involve fluorine atom addition from the matrix material to the appropriate interhalogen compound. A variety of matrix materials, including SF_6 , SiF_4 , MoF_6 , WF_6 , SeF_6 and Xe, have been examined in order to determine their ability to form and stabilize radical species. SF_6 was found to be the most versatile matrix material as the summarized esr data in Table II illustrate. It is interesting to note that the ClF_4 radical is formed with unusual ease by this technique and also that this method is considerably "cleaner" than the approach used

by Morton and Preston¹⁹ to produce ClF_4 . A radical originally thought to be SiF_5 formed in the γ -radiolysis of $\text{ClF}_3/\text{SiF}_4$ mixtures proved to be a small quantity of ClF_4 . The failure of such radicals as ClF_2 , BrF_4 , and IF_6 to be formed on γ -radiolysis of Cl_2/SF_6 , BrF_3/SF_6 , and IF_5/SF_6 mixtures, respectively, remains a mystery. The size of the matrix trapping sites may play a major role in the success of this particular method.

One problem which manifested itself from the onset of this work was the reaction of various interhalogen materials with the metal to glass seals used in attaching the quartz tubes to the metal vacuum line prior to the samples being sealed off. This problem was largely overcome through the use of FEP Teflon which has proven to be an excellent non-reactive containment material. The FEP Teflon tubes (1/8" o.d.) are attached to the vacuum line with standard Swagelok fittings and can be sealed readily with a "soft" flame. The Teflon also appears to be superior to the quartz as a containment material for the more reactive interhalogens, such as ClF_3O .

Table II. Summary of ESR Studies

Compound	Matrix ^a	Radicals Formed ^{b,c}
Cl ₂	SF ₆	X
ClF	SF ₆	X
ClF	Xe	X
ClF	SiF ₄	X
ClF ₃	SF ₆	ClF ₄
ClF ₃	SiF ₄	ClF ₄
ClF ₃	ClF ₃	X
ClF ₃ ^{d,e}	SF ₆	ClF ₄
ClF ₅	SF ₆	ClF ₄ , ClF ₆
ClF ₅	Xe	X
ClF ₅	ClF ₅	X
Br ₂	SF ₆	X
BrF ₃ ^d	SF ₆	X
BrF ₃	Xe	X
BrF ₅	SF ₆	BrF ₆
BrF ₅	Xe	X
BrI	SF ₆	X
IF ₅ ^d	SF ₆	X
IF ₅	Xe	X
IF ₅	SeF ₆	X
IF ₅	MoF ₆	X
SiF ₄	SF ₆	X
SF ₆	SF ₆	X
SiF ₄	SiF ₄	X
SiF ₄	Xe	X
XeOF ₄	SF ₆	X
SF ₄	SF ₄	X
SF ₄	SF ₆	X
NF ₃	SF ₆	X
MoF ₆ ^d	MoF ₆	X
WF ₆ ^d	SF ₆	X
OF ₂ ^d	SF ₆	X
WF ₆	WF ₆	X

^aAll mixtures were ~5 mole % and were prepared in Suprasil quartz tubes.

^bThe radicals SF₅ and SF₆⁻ were observed in mixtures containing SF₆.

^cX denotes no new radicals were formed.

^dMixtures also prepared in FEP Teflon tubes.

^eInfrared analysis of ClF₃O showed major contamination by ClF₃ and poor agreement with the published spectrum of ClF₃O.

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VIBRATIONAL SPECTRA OF THE BINARY FLUORIDES
OF THE MAIN GROUP ELEMENTS - A REVIEW

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Abstract. The results of vibrational spectroscopic studies on the fluorides of the main group elements are summarized in this review. Emphasis is placed on results obtained by matrix isolation. The trends in the periodic table are noted.

Vibrational spectroscopy is an important tool for the characterization of various chemical species. Valuable information regarding molecular structures as well as intra- and intermolecular forces can be extracted from vibrational spectral data. Recent advances, such as the introduction of laser sources to Raman spectroscopy, the commercial availability of Fourier transform infrared spectrometers, and the continuing development and application of the matrix-isolation technique to a variety of chemical systems, have greatly enhanced the utility of vibrational spectroscopy to chemists.

Inorganic fluorine compounds are of considerable interest and importance not only because fluorides of nearly all known elements, including some of the rare gases, have been synthesized, but because a number of these compounds are quite different from other halides. Consider, for example, the compounds SF_4 and SF_6 and their chloro analogs. SF_6 is chemically a very inert and a very stable compound while SF_4 , also quite stable, is quite reactive. The corresponding tetrachloride molecule is stable only at low temperatures while the hexachloride molecule is nonexistent.

Many fluorides, particularly the interhalogens, are very reactive and require special handling techniques. Matrix isolation has proven to be a very useful technique in the study of inorganic fluorides; it is particularly useful in the study of very reactive species, such as the free radicals and high-temperature vapor species. Such molecules can be stabilized in a low-temperature matrix environment which effectively prevents reaction with cell and window materials. Since the molecules are effectively isolated from each other, problems involving molecular association are minimized. There is generally a good correlation between matrix and gas phase spectral data except in cases where strong interaction between the matrix material and the isolated molecule exists. Narrow bandwidths are a characteristic

feature of matrix spectra making it frequently possible to obtain structural information from bands involving different isotopes. Matrix-isolation data will be utilized, wherever possible, throughout this paper.

In this review we summarize and attempt to correlate vibrational spectral data amassed from the literature for the main group inorganic binary fluorides. In addition, a brief review of the matrix-isolation studies of both reactive intermediates and high-temperature fluoride vapor species is included, placing particular emphasis on the interhalogen molecules.

A. Inorganic Binary Fluorides

In this section available vibrational data for the main group binary fluorides will be reviewed in an attempt to establish trends in both structures and bond stretching force constants. The review is restricted primarily to molecular entities which were observed either in the gas phase or in inert matrices. The emphasis on the matrix data in this review is in contrast with the more general approach taken by Reynolds in an earlier review of the vibrational spectra of inorganic fluorides (1).

Vibrational spectra, besides being utilized to establish molecular structures, can be used in the evaluation of molecular force constants. Considerable effort has been expended to relate bond stretching force constants to bond order. Although no specific theoretical model has been found that will cover all types of chemical bonds, there exists a qualitative relationship between bond stretching force constants and bond orders which permits a comparison of bond strengths for molecules such as the binary fluorides. In making such a comparison, a consistent force field model must be adhered to. The General Valence Force Field (GVFF) or an approximation of this field generally referred to as the Modified Valence Force Field (MVFF) are the potential models which have become increasingly popular

with chemists. Valence force constants normally exhibit good transferability between molecules possessing similar types of bonds. Valence stretching force constants further bear a close relationship to the chemical bonding forces. Force constants utilizing the valence force field were, therefore, chosen for comparison in this paper for the reasons just mentioned and because of the wealth of data available in the literature. Although a unique set of force constants rarely exists for a given polyatomic molecule, one preferred set can normally be chosen on a physical basis. Relating stretching force constants to bond energies should be treated with caution, particularly for molecules exhibiting a large percentage of ionic bonding, since the magnitude of the force constant is primarily a reflection of only the covalent character of a particular bond.

Table I lists the symmetry point groups and X-F stretching force constants for those main group binary fluorides for which the oxidation state of the element combined with fluorine corresponds to the group number. In Tables II-VI vibrational spectral data, (using matrix isolation results if available) including the X-F stretching force constants, are presented for the main group binary fluorides having formulas ranging from XF to XF_5 , respectively. Two force constant trends are apparent. First, the force constants decrease in magnitude from top to bottom for a given group in each of these tables with certain exceptions noted below. For molecules which possess both equatorial and axial X-F bonds, the axial stretching force constant exhibits the top to bottom trend opposite to that previously mentioned. Going from left to right the force constants in the periodic table first increase reaching a maximum in a given period somewhere in the vicinity of the transition point from metal to nonmetal; this is followed by a decrease in the force constant. These force constant trends are much more apparent for Tables I-III where a more complete set of data is available.

From the data presented in Tables I-VI, it appears that a particular structure is maintained for molecules of the same formula and within a given group with the exception of BeF_2 and MgF_2 which are linear while the remaining members of that group have bent (C_{2v}) structures. The vibrational data for the diatomic fluorides presented in Table II are taken from gas phase electronic and matrix-isolation spectral studies; both sets of data are available for a number of the diatomic molecules in this Table. The gas phase frequencies have all been corrected for anharmonicity except in the case of fluorine, this is apparently the reason for its force constant being lower than that for ClF . If the matrix data for the diatomic molecules of Group VIIA are examined, however, the expected top to bottom trend is observed. The apparent reversal in the magnitudes of the gas phase and matrix frequencies for MgF is a rather unusual occurrence which is also worth noting.

In Table III there are several points worthy of note. For both Groups VA and VIIIA there appear to be deviations from the apparent normal top to bottom trend with PF_2 and XeF_2 having slightly larger force constants than NF_2 and KrF_2 , respectively. All molecules in Table III have bent (C_{2v}) structures with the exception of KrF_2 and XeF_2 which are linear ($\text{D}_{\infty h}$) as are BeF_2 and MgF_2 , as previously noted, and the MF_2 molecules of Group IA which are apparently triangular (C_{2v}). For the series of molecules, CF_2 , NF_2 , and OF_2 , the ν_1 mode is observed to have a higher frequency than that for the ν_3 mode which is an apparent deviation from normal trends. This behavior may be a result of dynamic effects due to the similarity in the masses of the various atoms making up this series of triatomic molecules (2). The assignment of the ν_1 mode to a higher frequency value than ν_3 has been made for a number of other molecules in this Table. In some cases, however, these assignments are subject to some uncertainty. Raman data, which could be

utilized to clarify such situations, are largely unavailable for molecules in Table III since the majority of the data come from infrared matrix-isolation studies.

In Table IV NF_3 appears to be an exception as its stretching force constant is lower than that for PF_3 . It should be noted also that the force constants for CF_3 and SiF_3 are very nearly the same. The XF_3 compounds of group VIIA possess two equivalent axial X-F bonds and one equatorial or unique bond. The equatorial type bonds are stronger than the axial bonds for all molecules in Tables IV-VI which exhibit bonding of this type with the exception of the XF_5 molecules of Group VIIA. The range of point group symmetry for the molecules in Table III is D_{3h} for Group IIIA, C_{3v} for Groups IVA and VA, C_s for Group VIA, and C_{2v} for Group VIIA. The frequency data for Group VA indicate that ν_1 is greater than ν_3 for each member of that series.

Vibrational data for the main group binary fluorides with the formula XF_4 are restricted to compounds of Groups IVA, VIA, and VIIIA as exemplified in Table V. Molecules of Group VIA possess two axial and two equatorial X-F bonds. The range of point group symmetry for the molecules in Table V is T_d for Group IVA, C_{2v} for Group VIA, and D_{4h} for Group VIIIA.

The XF_5 molecules of Group VIIA possess C_{4v} symmetry and have four equivalent equatorial X-F bonds and one unique axial bond as indicated in Table VI. The equatorial stretching force constant exhibits the reverse of the normal top to bottom trend previously noted for bonds of this type. The XF_5 molecules of Group VA have D_{3h} symmetry. It appears appropriate at this point to present a brief discussion of SbF_5 , since there has been considerable uncertainty in the interpretation of the vibrational spectra and the assignment of a structure to the monomer. A recent report involving a temperature dependent study of the Raman gas phase spectrum of SbF_5 (3) indicates that previous vibrational assignments were apparently in error. This

study shows that SbF_5 is strongly associated in the gas phase even at temperatures as high as 250°C . The association apparently occurs through bonds involving cis-fluorine bridging. An assignment of a C_{4v} structure to the monomer for SbF_5 from a previous matrix-isolation study (4) appears to be negated, since the experimental conditions which were utilized could not preclude the predominance of the associated species. The force constants presented in Table VI for SbF_5 are based upon an incorrect vibrational assignment. It would appear, however, that a corrected assignment might produce very little effect on magnitudes of these reported stretching force constants, and so they are included for comparison.

Vibrational data for various isoelectronic binary fluorides with the formula XF_4 are listed in Table VII. For the first series in the upper left of this table, the force constant increases in going from BF_4^- to CF_4 and then decreases slightly for NF_4^+ . It would appear that the next series beginning with AlF_4^- would follow a similar trend except data for PF_4^+ are unavailable. The fluorides of these two series all have T_d symmetry. Very little can be said in regard to the three series in the lower right section of the Table since the data are largely incomplete. The symmetry, however, for the various species in these series is C_{2v} .

Vibrational data are presented in Table VIII for various isoelectronic series of the formula XF_6 . All the species in the Table possess O_h symmetry. The left to right horizontal force constant trends are similar for each of these series, as the magnitudes are observed to increase to Group VIA and then decrease slightly for Group VIIA. The exception to this particular trend occurs in the lower series which increases continuously from left to right. There is a general decrease in the force constants in going from top to bottom for all groups in this table with the exception of VIIA which exhibits the reverse trend.

In the compilation of force constant data for the inorganic binary fluorides, it would be of interest to examine how bonding of additional atoms such as oxygen might affect the bond strengths of selected X-F bonds. Vibrational data have been compiled in Table IX for NF, ClF, NF₃, and ClF₃ along with various oxygenated forms of these compounds to illustrate this effect. The N-F and Cl-F stretching force constants are observed to be reduced to approximately one half of their original values in going from NF to FNO and from ClF to FClO, respectively. Further addition of oxygen atoms in both series appears to have little effect on the corresponding X-F stretching force constants, except for an eventual slight increase over the value for the mono-oxygenated species. The N-F stretching force constant is essentially unaffected in going from NF₃ to NF₃O while the Cl-F force constants are mildly reduced from ClF₃ to ClF₃O. The force constant for the unique bond of ClF₃O exhibits a much larger reduction than that for the axial bonds. On addition of a second oxygen atom to yield the molecule ClF₃O₂, both unique and axial force constants increase over the values for ClF₃O, with latter force constant having a value equal to that of ClF₃.

Of interest is also the effect additional electrons have on the structures and stretching force constants for a given fluoride series having the same molecular formula. This effect is illustrated in Table X for the ClF₂⁺, ClF₂, and ClF₂⁻ series. The structures range from bent (C_{2v}) for ClF₂⁺ and ClF₂ with bond angles of 100° and ~150°, respectively, to linear (D_{∞h}) for ClF₂⁻. The stretching force constants for ClF₂ and ClF₂⁻ are 2.48 and 2.35 mdyn/Å, respectively, which is approximately half the value for that of ClF₂⁺ and indicates that the additional electrons for ClF₂ and ClF₂⁻ are largely antibonding. A more complete discussion of ClF₂ will be made in the following section.

In concluding this section a list of other main group binary fluorides for which there are either complete or partial vibrational data available is presented in Table XI.

B. Matrix-Isolation Studies of Transient Inorganic Binary Fluoride Species

The area in which matrix isolation is perhaps of greatest value is the stabilization of transient species such as free radicals and high temperature vapors. Until quite recently infrared spectroscopy was utilized almost exclusively for the vibrational studies of matrix-isolated species. With the introduction of laser sources and the development of more sensitive electronic light detection systems, Raman matrix-isolation studies are now feasible and have recently been applied to a limited number of unstable inorganic fluoride species including the molecules OF (5) and ClF₂ (6). Both of these species were formed for Raman study by a novel technique which utilizes the 4880 Å output from an Ar ion laser as both the photolysis source and the Raman excitation source. The examples of ClF₂ (6), GeF₂ (7), and MgF₂ (8) illustrate the complementary data that Raman matrix-isolation spectroscopy can provide. Other binary fluoride molecules for which Raman matrix data is available include OF₂ (5), MF₂ and MF₃ (M=alkali metals) (9,10), S₂F₁₀ (11), KrF₂ and XeF₂ (5), with the latter two molecules having been formed by the same laser photolysis method as previously mentioned. Raman matrix-isolation spectroscopy has recently been reviewed by Ozin (12), and although merely in the early stages of development, it is anticipated that this area will continue to grow and become a valuable counterpart to the infrared technique.

This section represents a brief review of matrix-isolation studies of the main group binary fluoride free radicals and high-temperature vapor species. A discussion of the halogen fluoride molecules will be stressed since this is an area of considerable interest to our laboratory. A list of main group binary fluorides which have been characterized by matrix-isolation appears in Table XII. It is apparent from this Table that there are large gaps in the existing data for such species as the halogen fluoride

radicals which must be filled in order to gain a better understanding of the structural properties and bonding which are characteristic of these systems. Presently ClF_2 and Cl_2F are the only halogen fluoride radicals for which vibrational data have been published. The ClF_4 (13,14), ClF_6 (14,15), BrF_6 (15,16), and IF_6 (15) radicals have recently been prepared by γ -radiolysis and characterized by esr although no vibrational spectroscopic data are available. Other interhalogen radicals, Cl_3 and Br_3 , which were reportedly formed by microwave discharge (17,18) may in fact be the ionic X_3^- species (19).

The ClF_2 radical is of sufficient chemical significance to merit a brief discussion. This particular radical is an interesting species due to the fact that it possesses 21 valence electrons and appears to have an intermediate bond angle of $\sim 150^\circ$. Such a bond angle is apparently unique for interhalogen species since the bond angles for most of these molecules are very near 90° or 180° . The ClF_2 radical was first prepared in our laboratory through the matrix reaction $\text{ClF} + \text{F} \rightarrow \text{ClF}_2$ (20). This reaction was initiated by production of F-atoms through in situ u.v. photolysis of molecular fluorine. From the infrared data the three vibrational fundamentals were assigned. On this basis and on the basis of ^{35}Cl , ^{37}Cl isotopic shift data for ν_3 , ClF_2 was assigned a bent (C_{2v}) structure with a bond angle of $\sim 135^\circ$. Very recently, however, Andrews' group (6) has repeated the infrared work and in addition has successfully prepared ClF_2 by the laser photolysis technique for Raman study. Bases upon the new Raman data, the ν_1 mode was reassigned from a value of 536 cm^{-1} to that of 500 cm^{-1} . It appears that the principle of mutual exclusion holds for the ClF_2 radical which is indicative of a linear triatomic species, but as Andrews points out, mutual exclusion is valid only within the limits of detectability, which may be a problem for weakly active modes in dilute matrices. In a

reassessment of the data, Andrews favors a slightly bent structure with a bond angle of $\sim 150^\circ$.

Recently we have completed (in collaboration with E. S. Prochaska and L. Andrews of the University of Virginia) a matrix isolation study of the bromine-fluorine system (21). Evidence for the formation of BrF_2 , Br_2F , and Br_2F_2 was obtained. These experiments involved UV-photolysis of matrix mixtures, including BrF_3 in Ar, equilibrium mixtures of BrF , BrF_3 , and Br_2 in Ar, alone and codeposited with F_2 in Ar, and Br_2 in Ar and F_2 in Ar deposited from separate manifolds. Also microwave discharge experiments were done with samples of Ar/Br_2 and Ar/F_2 mixed before and during discharge. The microwave experiments were stimulated by a recent mass spectrometric kinetic study (22) which appeared to present a method producing BrF in a much purer form. The data for BrF_2 are of considerable interest for the purposes of comparison with ClF_2 . A doublet near 569 cm^{-1} with a 2.2 cm^{-1} isotopic splitting was attributed to BrF_2 , and a calculation of $152^\circ \pm 8^\circ$ for the lower limit of the F-Br-F valence angle strongly indicates that, like ClF_2 , BrF_2 is also obtusely bent. Bands observed at 555 and 507 cm^{-1} were attributed to Br_2F_2 and Br_2F , respectively, based upon photolysis behavior similar to their chlorine analogs.

Vibrational data for the majority of the molecules in Table XII were presented in the first section and these species will not be discussed further.

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Table I. Stretching Force Constants And Symmetry For Main Group Binary Fluorides

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
$\text{LiF}^* (23, 24)^b$	$\text{BeF}_2^* (26)$	$\text{BF}_3^* (29, 30)$	$\text{CF}_4^* (33, 34)$	--	--	--	--
Sym. $C_{\infty v}$	$D_{\infty h}$	D_{3h}	T_d				
K_{F-X}^a 2.12	5.15	7.29	6.70				
$\text{NaF}^* (9)$	$\text{MgF}_2^* (8, 27, 28)$	$\text{AlF}_3^* (31, 32)$	$\text{SiF}_4^* (35, 36)$	$\text{PF}_5 (39)$	$\text{SF}_6^* (40, 41)$	--	--
Sym. $C_{\infty v}$	$D_{\infty h}$	D_{3h}	T_d	D_{3h}	O_h		
K_{F-X} 1.51	3.23	4.91	6.11	6.32 ^c , 4.47 ^d	5.26		
$\text{KF}^* (25)$	$\text{CaF}_2^* (27)$	--	$\text{GeF}_4^* (37, 38)$	$\text{AsF}_5^* (4, 39)$	$\text{SeF}_6 (42)$	--	--
Sym. $C_{\infty v}$	C_{2v}		T_d	D_{3h}	O_h		
K_{F-X} 1.18	2.21		5.45	5.47 ^c , 4.51 ^d	5.01		
$\text{RbF}^* (9)$	$\text{SrF}_2^* (27)$	--	--	$\text{SbF}_5^* (3, 4, 39)$	$\text{TeF}_6 (43)$	$\text{IF}_7 (44, 45, 46)$	--
Sym. $C_{\infty v}$	C_{2v}			D_{3h}	O_h	D_{5h}	
K_{F-X} 1.01	1.97			5.38 ^c , 4.75 ^d	5.07	3.01 ^c , 4.10 ^d	
$\text{CsF}^* (9)$	$\text{BaF}_2^* (27)$	--	--	--	--	--	--
Sym. $C_{\infty v}$	C_{2v}						
K_{F-X} 0.95	1.59						

* Matrix data available.

a. Units for force constants in $\text{mdyn}/\text{\AA}$.

b. References in parentheses.

c. Equatorial fluorine atoms.

d. Axial fluorine atoms.

Table II. Vibrational Data for Main Group Binary Fluorides With Formula XF

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
K _F -X ^a ω_e	LiF (23,24,47) ^b	BeF (47)	BF (47)	CF (53)	NF (55,56)	OF (5,25,59)	F ₂ (6,47)
	2.48 2.12*	5.77	8.05	7.09*	6.18 5.90*	5.42*	4.45 ^d 4.43*
	906 840* [Ar] ^c	1266	1400	1279* [Ar]	1141 1115* [Ar]	1029* [Ar]	892 ^d 890* [N ₂]
K _F -X ω_e	NaF (9,47)	MgF (47,48)	AlF (31,47)	SiF (54)	PF (57)	--	ClF (6,47)
	1.76 1.51*	3.22 3.41*	4.36 4.05*	4.91	4.98		4.56 4.24*
	536 496* [Ar]	718 738* [Kr]	815 785* [Ne]	858	847		793 764* [N ₂]
K _F -X ω_e	KF (25,47)	CaF (47)	GaF (49,50)	GeF (47)	AsF (58)	--	BrF (47,60)
	1.37 1.18*	2.62	3.25*	3.93	4.20		4.07 3.93*
	426 396* [Ar]	587	609* [Ne]	665	686		671 660* [Ar]
K _F -X ω_e	RbF (9,47)	SrF (47)	InF (51)	SnF (47)	SbF (47)	--	IF (61)
	1.30 1.01*	2.30	2.75	3.28	3.65		3.62
	376 332* [Ar]	500	535	583	614		610
K _F -X ω_e	CsF (9,47)	BaF (47)	TlF (47,52)	PbF (47)	BiF (47)	--	--
	1.22 0.95*	2.16	2.31 1.99*	2.64	2.68		
	353 312* [Ar]	469	475 441* [Ar]	507	511		

* Matrix data.

^a Force constant units in mdyn/Å and frequency units in cm⁻¹.^b References in parentheses.^c Matrix material indicated within brackets.^d Uncorrected for anharmonicity.

Table III. Vibrational Data For Main Group Binary Fluorides With Formula XF₂

	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Sym.	⁶ LiF ₂ [*] (9) ^b C _{2v}	BeF ₂ [*] (26) D _{∞h}	CF ₂ [*] (33) C _{2v}	NF ₂ [*] (33, 65, 66) C _{2v}	OF ₂ [*] (5, 25) C _{2v}	--	--
K _F -X ^a	--	5.15	6.00	4.83	4.10	--	--
Obs. Freq.	^a ν ₁ -452 ν ₂ -708 [Ar] ^c	ν ₂ -330 ν ₃ -1542 [Ne]	ν ₁ -1222 ν ₂ -668 ν ₃ -1102 [Ar]	ν ₁ -1070 ν ₂ -573 ν ₃ -931 [N ₂]	ν ₁ -925 ν ₂ -446 ν ₃ -826 [Ar]	--	--
Sym.	NaF ₂ [*] (9) C _{2v}	MgF ₂ [*] (8, 27, 28) D _{∞h}	SiF ₂ [*] (37, 62) C _{2v}	PF ₂ [*] (36) C _{2v}	SF ₂ [*] (67) C _{2v}	ClF ₂ [*] (6, 20) C _{2v}	--
K _F -X	--	3.23	4.90	4.93	--	2.48	--
Obs. Freq.	ν ₁ -475 ν ₂ -454 [Ar]	ν ₁ -550 ν ₂ -249 ν ₃ -842 [Ar]	ν ₁ -843 ν ₂ -343 ν ₃ -855 [Ar]	ν ₁ -831 ν ₃ -852 [Ar]	ν ₃ -847 [Ar]	ν ₁ -500 ν ₂ -242 ν ₃ -578 [N ₂]	--
Sym.	KF ₂ [*] (9) C _{2v}	CaF ₂ [*] (27) C _{2v}	GeF ₂ [*] (7, 37) C _{2v}	--	--	BrF ₂ [*] (22) C _{2v}	KrF ₂ [*] (5, 68, 69) D _{∞h}
K _F -X	--	2.21	4.16	--	--	--	2.46
Obs. Freq.	ν ₁ -464 ν ₂ -342 [Ar]	ν ₁ -485 ν ₂ -163 ν ₃ -554 [Kr]	ν ₁ -685 ν ₂ -263 ^e ν ₃ -653 [Ne, N ₂]	ν ₃ -64	ν ₃ -569 [Ar]	--	ν ₁ -452 ν ₂ -236 ν ₃ -580 [Ar, Xe]
Sym.	RbF ₂ [*] (9) C _{2v}	SnF ₂ [*] (27) C _{2v}	--	--	--	--	XeF ₂ [*] (5, 68, 69) D _{∞h}
K _F -X	--	1.97	3.41	--	--	--	2.84
Obs. Freq.	ν ₁ -462 ^d ν ₂ -266 [Ar]	ν ₁ -441 ν ₂ -82 ν ₃ -442 [Kr]	ν ₁ -605 ν ₂ -201 ν ₃ -584 [Ne]	ν ₃ -64	--	--	ν ₁ -512 ^f ν ₂ -213 ν ₃ -547 [Ar, Xe]
Sym.	CsF ₂ [*] (9) C _{2v}	BaF ₂ [*] (27) C _{2v}	PbF ₂ [*] (63, 64) C _{2v}	--	--	--	--
K _F -X	--	1.59	2.92	--	--	--	--
Obs. Freq.	ν ₁ -459 ^d ν ₂ -248 [Ar]	ν ₁ -390 ν ₃ -413 [Kr]	ν ₁ -546 ν ₂ -170 ν ₃ -523 [Ne]	--	--	--	--

^a Matrix data available.^b Stretching force constant units in mdyn/Å and frequency units in cm⁻¹.^c Matrix material indicated in brackets.^d These assignments subject to uncertainty.^e Estimated from electronic spectra.^f Gas phase frequency.

Table V. Vibrational Data For Main Group Binary Fluorides With Formula XF₄

	IVA	V	VIA	VIIA	VIIIA
Sym.	CF ₄ [*] (33, 34, 80) ^b	--	--	--	--
KF-X ^a	T _d				
Obs. Freq.	6.70				

	ν_1 -909 ^c ν_3 -1267 [Ar] ^d				
	ν_2 -435 ^c ν_4 -631				
Sym.	SiF ₄ [*] (35, 36, 81)	--	SF ₄ [*] (77, 83, 84)	--	--
KF-X	T _d		C _{2v}		
	6.11		5.51 ^e , 3.30 ^f		
	---		---		
Obs. Freq.	ν_1 -800 ^c ν_3 -1022 [Ar]		ν_1 -884 ^c ν_4 -228 ^c ν_7 -529 [Ar, N ₂]		
	ν_2 -268 ^c ν_4 -384		ν_2 -552 ^c ν_4 -474 ^c ν_7 -858		
			ν_3 -360 ^c ν_6 -707 ^c ν_9 -357		
Sym.	GeF ₄ [*] (37, 38, 82)	--	SeF ₄ [*] (85)	--	--
KF-X	T _d		C _{2v}		
	5.45		5.04 ^e , 3.38 ^f		
	---		---		
Obs. Freq.	ν_1 -740 ^c ν_3 -799 ^c ν_4 -260 ^c [Ne]		ν_1 -743 ^c ν_4 -160 ^c ν_7 -723 [N ₂]		
	ν_2 -200 ^c ν_4 -260 ^c		ν_2 -589 ^c ν_5 -596 ^c ν_8 -254		
			ν_3 -406 ^c ν_7 -364		
Sym.	SnF ₄ [*] (64)	--	TeF ₄ [*] (85)	--	XeF ₄ [*] (69, 86, 87)
KF-X	T _d		C _{2v}		D _{4h}
	---		4.62 ^e , 3.53 ^f		3.00
Obs. Freq.	ν_3 -687 [Ar]		ν_1 -695 ^c ν_6 -587 [N ₂]		---
			ν_2 -572 ^c ν_7 -273		ν_1 -554 ^c ν_4 -216 ^c , ν_7 -161 ^c , ν_8
			ν_3 -333 ^c ν_8 -682		ν_2 -290 ^c ν_5 -524 ^c [Ar]
					ν_3 -218 ^c ν_6 -568
Sym.	PbF ₄ [*] (64)	--	---	--	--
KF-X	T _d				

Obs. Freq.	ν_3 -663 [Ar]				

* Matrix data available.

^a Stretching force constant units in mdyn/Å and frequency units in cm⁻¹.^b References in parentheses.^c Gas phase frequencies.^d Matrix material indicated in brackets.^e Equatorial fluorine atoms.^f Axial fluorine atoms.^g Evaluated from overtone observed in the Raman spectrum.

Table VI. Vibrational Data For the Main Group Binary Fluorides With Formula XF_5

	VA ^b	VIA	VIIA	VIIIA
Sym.	PF ₅ (39, 88) ^c	SF ₅ [*] (89)	ClF ₅ [*] (90, 91)	--
K _T -X ^a	D _{3h} ^d	C _{4v}	C _{4v}	--
	6.32 ^d , 4.47 ^e	--	2.75, 3.66 ^h	
Obs. Freq. ^a	--	--	--	--
	v ₁ -817 ^f v ₄ -576 ^f v ₇ -175 ^f	v ₇ -812 v ₈ -552 [Ar]	v ₁ -722 v ₄ -480 ^f v ₈ -482	
	v ₂ -640 ^f v ₅ -1026 ^f v ₈ -514		v ₁ -539 v ₄ -375 ^f v ₉ -299[N ₂]	
	v ₃ -945 ^f v ₆ -533 ^f		v ₂ -493 v ₇ -726	
Sym.	AsF ₅ [*] (4, 39, 88)	--	BrF ₅ [*] (77, 78, 91)	--
K _T -X	D _{3h} ^d		C _{4v}	
	5.47 ^d , 4.51 ^e		3.26, 4.01 ^h	
Obs. Freq.	--	--	--	--
	v ₁ -734 ^f v ₄ -397 v ₇ -130 ^f		v ₁ -681 v ₄ -535 ^f v ₈ -415	
	v ₂ -644 ^f v ₅ -808 ^f v ₈ -366 [Ar] ^g		v ₁ -582 v ₄ -312 ^f v ₉ -240 [Ar]	
	v ₃ -782 v ₆ -372 ^f		v ₂ -366 v ₇ -636	
Sym.	SbF ₅ [*] (3, 4, 39)	--	IF ₅ (91)	--
K _T -X	D _{3h} ^d		C _{4v}	
	5.38 ^d , 4.75 ^e		3.64, 4.68 ^h	
Obs. Freq.	--	--	--	--
			v ₁ -698 ^f v ₄ -575 ^f v ₈ -374 ^f	
			v ₂ -593 ^f v ₆ -273 ^f v ₉ -189 ^f	
			v ₃ -315 ^f v ₇ -640 ^f	

* Matrix data available.

^a Stretching force constant units in mdyn/Å and frequency units in cm⁻¹.

^b See text for a discussion of SbF₅.

^c References in parentheses.

^d Equatorial fluorine atoms.

^e Axial fluorine atoms.

^f Gas phase frequencies.

^g Matrix material indicated in brackets.

^h Unique fluorine atom.

Table VII. Vibrational Data For Various Isoelectronic Binary Fluoride Series With Formula XF_4

	IIIA	IVA ^e	VA	VIA ^e	VIIA
Sym.	PF_4^- (34, 92, 93) ^b	CF_4 (33, 34, 80)	NF_4^+ (95, 96)	--	--
$\text{K}_\text{F-X}$ ^a	T_d 4.57	T_d 6.70	T_d 6.06	--	--
Obs. Freq.	ν_1 -769 ν_3 -1084 ^c [Aqueous] ν_2 -353 ν_4 -524 [Sol.]	ν_1 -849 ν_3 -1162 [Solid] ν_2 -450 ν_4 -611 [NF ₄ BF ₄]	--	--	--
Sym.	AlF_4^- (94)	SiF_4 (35, 36, 81)	--	SF_4 (77, 83, 84)	ClF_4^+ (84, 97)
$\text{K}_\text{F-X}$	T_d 4.33	T_d 6.11	--	C_{2v} 5.51 ^f , 3.30 ^g	C_{2v} 4.78 ^f , 3.73 ^g
Obs. Freq.	ν_1 -622 ν_3 -760 [NF-AlF ₃] ν_2 -210 ν_4 -322 [Melts]	--	--	ν_1 -800 ν_4 -250 ν_7 -515 [ClF ₅ ·AsF ₅] ν_2 -571 ν_5 -475 ν_8 -829 [ClF ₅ ·SbF ₅] ν_3 -385 ν_6 -795 ν_9 -385 [Adducts]	ν_1 -800 ν_4 -250 ν_7 -515 [ClF ₅ ·AsF ₅] ν_2 -571 ν_5 -475 ν_8 -829 [ClF ₅ ·SbF ₅] ν_3 -385 ν_6 -795 ν_9 -385 [Adducts]
Sym.	--	--	--	SeF_4 (85)	BrF_4^+ (97)
$\text{K}_\text{F-X}$	--	--	--	C_{2v} 5.04 ^f , 3.38 ^g	C_{2v} ---
Obs. Freq.	--	--	--	--	--
Sym.	--	--	SbF_4^- (76)	TeF_4 (85)	IF_4^+ (97)
$\text{K}_\text{F-X}$	--	--	C_{2v} 3.3 ^f , 2.0 ^g	C_{2v} 4.62 ^f , 3.53 ^g	C_{2v} ---
Obs. Freq.	--	--	ν_1 -596 ν_4 -163 ν_7 -257 [MeCN] ν_2 -449 ν_5 -220 ν_8 -566 [Sol.] ν_3 -285 ν_6 -431 ν_9 -180	--	ν_1 -704 ν_4 -151 ν_8 -720 [IF ₅ ·SbF ₅] ν_2 -609 ν_5 -655 ν_9 -316 [Adduct] ν_3 -341 ν_7 -385

^aStretching force constant units in mdyn/Å and frequency units in cm⁻¹.^bReferences in parentheses.^cKBr matrix value.^dThe state for which the frequencies were observed is denoted in brackets.^eObserved frequencies given in Table V.^fEquatorial fluorine atoms.^gAxial fluorine atoms.

Table VIII. Vibrational Data For Various Isoelectric Binary Fluoride Series of Formula XF_6

	IIIA	IVA	VA	VIA	VIIA
Sym.	AlF_6^{3-} (98) ^b	SiF_6^{2-} (99)	PF_6^- (43)	SF_6 (40, 100, 101)	ClF_6^+ (40)
$\text{K}_2\text{F-X}^a$	O_h	O_h	O_h	O_h	O_h
	--	3.01	4.39	5.26	4.68
Obs. Freq.	v_1 -555 v_5 -345 ^c [MF-AlF ₃] ^c	v_1 -663 v_4 -483 [Solid]	v_1 -746 v_4 -557 [PF ₆]	v_1 -774 v_4 -614 [Gas]	v_1 -679 v_4 -582 [Solid]
	v_2 -390 [Melts]	v_2 -477 v_5 -408 [Na ₂ SiF ₆]	v_2 -561 v_5 -475 [Salt]	v_2 -642 v_5 -525	v_2 -630 v_5 -513 [ClF ₆ PF ₆]
		v_3 -741	v_3 -817	v_3 -939	v_3 -690
Sym.	--	GeF_6^{2-} (99)	AsF_6^- (43)	SeF_6 (42, 100, 101)	BrF_6^+ (43, 102)
$\text{K}_2\text{F-X}$	O_h	O_h	O_h	O_h	O_h
	2.71	3.98	3.98	5.01	4.90
Obs. Freq.	v_1 -624 v_4 -359, 339	v_1 -682 v_4 -385 [Solid]	v_1 -682 v_4 -385 [Solid]	v_1 -707 v_4 -437 [Gas]	v_1 -658 v_4 -430 [Solid]
	v_2 -471 v_5 -335 [Solid]	v_2 -568 v_5 -369 [BrF ₆ AsF ₆]	v_2 -568 v_5 -369 [BrF ₆ AsF ₆]	v_2 -659 v_5 -405	v_2 -668 v_5 -405 [BrF ₆ AsF ₆]
	v_3 -603	v_3 -696	v_3 -696	v_3 -720	v_3 -775
Sym.	--	SnF_6^{2-} (99)	SbF_6^- (43)	TeF_6 (43, 100, 101)	IF_6^+ (43, 103)
$\text{K}_2\text{F-X}$	O_h	O_h	O_h	O_h	O_h
	2.77	3.90	3.90	5.07	5.42
Obs. Freq.	v_1 -592 v_4 -300 [Solid]	v_1 -653 v_4 -280 [Solid]	v_1 -653 v_4 -280 [Solid]	v_1 -697 v_4 -325 [Gas]	v_1 -708 v_4 -343 [Solid]
	v_2 -477 v_5 -252 [Na ₂ SnF ₆]	v_2 -561 v_5 -273 [BrF ₆ SbF ₆]	v_2 -561 v_5 -273 [BrF ₆ SbF ₆]	v_2 -670 v_5 -314	v_2 -732 v_5 -340 [IF ₆ AsF ₆]
	v_3 -559	v_3 -667	v_3 -667	v_3 -752	v_3 -794

^a Stretching force constant units in mdyne/Å and frequency units in cm⁻¹.

^b References in parentheses.

^c The state for which the frequencies were observed is denoted in brackets.

Table IX. Vibrational Data For Selected Nitrogen And Chlorine Fluorides Containing Oxygen

NF Compound	F-X			F-X			Stretching Force Constant (mdyn/Å)
	Symmetry	Observed Frequencies (cm ⁻¹)	Stretching Force Constant (mdyn/Å)	Compound	Symmetry	Observed Frequencies (cm ⁻¹)	
NF [*] (55,56) ^{a,b}	C _{∞v}		5.90	ClF [*] (6,47) ^b	C _{∞v}		4.24
ENO (104)	C _s	ν ₁ -1877 ν ₂ -775 [Gas] ^d ν ₃ -521	2.26	FCIO [*] (108)	C _s	ν ₁ -1038 ν ₂ -594 Ar ν ₃ -315 [Matrix]	2.59
ENO ₂ (105)	C _{2v}	ν ₁ -1310 ν ₄ -1792 ν ₂ -822 ν ₅ -560 [Gas] ν ₃ -569 ν ₆ -742	2.66	FCIO ₂ (109)	C _s	ν ₁ -1106 ν ₄ -402 ν ₂ -630 ν ₅ -1271 [Gas] ν ₃ -547 ν ₆ -351	2.53
NF ₃ [*] (72,73) ^c	C _{3v}		4.16	ClF ₃ [*] (77) ^c	C _{3v}	ν ₁ -1061 ν ₄ -1315 ν ₂ -715 ν ₅ -589 [Gas] ν ₃ -549 ν ₆ -405	2.79
NF ₃ O (106,107)	C _{3v}	ν ₁ -1689 ν ₄ -880 ν ₂ -740 ν ₅ -522 [Gas] ν ₃ -534 ν ₆ -398	4.25	ClF ₃ O [*] (112)	C _s	ν ₁ -1223 ν ₄ -478 ν ₂ -686 ν ₅ -323 ^f ν ₃ -484 ν ₆ -224 ^f	4.19 ^f , 2.70 3.16 ^f , 2.34
				ClF ₃ O ₂ [*] (113)	C _{2v}	ν ₁ -1093 ν ₅ -287 ν ₂ -683 ν ₆ -417 ν ₃ -519 ν ₇ -686 ν ₄ -487 ν ₈ -591	3.35 ^f , 2.70 3.35 ^f , 2.70

* Matrix data available.

a References in parentheses.

b Observed frequencies given in Table II.

c Observed frequencies given in Table IV.

d The state for which the frequencies were observed is denoted in brackets.

e Gas phase frequency.

f Unique fluorine atom.

Table X. Vibrational And Structural Data For ClF_2^n ($n = +1, 0, -1$) Series

ClF_2 Species	Symmetry	Observed Frequencies (cm^{-1})	Bond Angle	F-Cl Stretching	
				Force Constant (mdyn/\AA)	
ClF_2^+ (6,114,115) ^a	C_{2v}	ν_1 -807 [Solid] ^c ν_2 -337 [$\text{ClF}_2^+\text{SbF}_6^-$] ν_3 -830	100°	4.74	
ClF_2 (6,20) ^b	C_{2v}		~150°	2.48	
ClF_2^- (116)	$D_{\infty h}$	ν_1 -476 ν_3 -635 [Solid - $\text{Na}^+\text{ClF}_2^-$ $\text{Rb}^+\text{ClF}_2^-$]	180°	2.35	

^aReferences in parentheses.

^bObserved Frequencies given in Table III.

^cThe state for which the frequencies were observed is denoted in brackets.

Table XI. Listing of Other Binary Fluorides For Which Vibrational Data Are Available

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
(LiF) ₂ [*] [24,117] ^a	BeF ₄ ²⁻ [120]	B ₂ F ₄ [*] [121]	C ₂ F ₄ [*] [33,123]	N ₂ F ⁺ [126]	O ₂ F ₂ [*] [134,135]	F ₃ ^{-*} [10]	
(LiF) ₃ [*] [118]		(BF ₃) ₂ [*] [29]	C ₂ F ₆ [*] [33,124]	N ₂ F ₂ [*] [56,127,128]	O ₄ F ₂ [*] [136]		
				N ₂ F ₃ ⁺ [129]			
				N ₂ F ₄ [*] [65,130,131]			
				N ₃ F [*] [56]			
(NaF) ₂ [*] [9,119]	(MgF ₂) ₂ [*] [8,28]	(AlF) ₂ [*] [31,49]	Si ₂ F ₆ [125]	P ₂ F ₄ [*] [36,132,133]	S ₂ F ₁₀ [*] [11,137,138]	ClF ₄ ⁻ [142]	
		(AlF ₃) ₂ [*] [31,122]		PF ₃ =PF [*] [36]	S ₂ F ₂ [139]	Cl ₂ F ₂ ⁺ [143,144]	
					(SF ₄) ₂ [*] [77]	Cl ₂ F [*] [145]	
					S ₂ F ₄ [140]	Cl ₂ F ₂ [*] [145]	
					SF ₅ ⁻ [141]	Cl ₂ F ₃ [*] [145]	
						(ClF ₃) ₂ [*] [145]	
(KF) ₂ [*] [9]	--	(GaF) ₂ [*] [49]	(GeF ₂) ₂ [*] [7,37]	--	(SeF ₄) ₂ [*] [85]	BrF ₂ ⁺ [115]	KrF [*] [147]
		(GaF ₃) ₂ [*] [49]			SeF ₅ ⁻ [141]	BrF ₄ ⁻ [142]	KrF ⁺ [148,149]
						Br ₂ F [*] [22]	Kr ₂ F ₃ ⁺ [149]
						Br ₂ F ₂ [*] [22]	
						(BrF ₃) ₂ [*] [77]	
(RbF) ₂ [*] [9]	--	--	--	SbF ₅ ²⁻ [76]	TeF ₅ ⁻ [76,141]	IF ₄ ⁻ [142]	XeF [*] [147]
				Sb ₂ F ₁₁ ⁻ [102]	Tc ₂ F ₁₀ [137]	IF ₆ ⁻ [146]	XeF ⁺ [150]
					(TeF ₄) ₂ [*] [85]	IF ₆ ³⁻ [142]	Xe ₂ F ₃ ⁺ [150]
(CsF) ₂ [*] [9]	--	(TlF) ₂ [*] [52]	--	--	--	--	XeF ₆ [*] [151]

^aMatrix data available.
References in brackets.

Table XII. Inorganic Binary Fluoride Free Radicals, Intermediates, and High-Temperature Vapor Species Characterized By Matrix Isolation

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
LiF [23,24] ^a	BeF ₂ [26]	---	CF [53]	NF [56]	OF [5,23,59]	--	--
			CF ₂ [33]	NF ₂ [33,65]	O ₂ F [134,136]		
			CF ₃ [33]				
NaF [9,119]	MgF [48]	AlF [31]	SiF ₂ [37,62]	PF ₂ [36]	SF ₂ [67]	ClF ₂ [6,20]	--
	MgF ₂ [8,27,28]	AlF ₃ [31,32]	SiF ₃ [71]		SF ₃ [67]	Cl ₂ F [145]	
					SF ₅ [89]		
KF [9]	CaF ₂ [27]	GaF [49,50]	GeF ₂ [7,37]	--	--	BrF ₂ [22]	--
		GaF ₃ [49]				Br ₂ F [22]	
--	SrF ₂ [27]	--	SnF ₂ [63,64]	SbF ₃ [76]	--	--	--
			SnF ₄ [64]				
--	BaF ₂ [27]	TlF [52]	PbF ₂ [63,64]	--	--	--	--
			PbF ₄ [64]				

^aReferences in brackets.

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The Chlorine Hexafluoride Radical. Preparation, Electron Spin Resonance Spectrum, and Structure¹

Sir:

Chlorine hexafluoride is the only unreported molecule of the series ClF_n ($n = 1-6$) to date. This hypervalent radical possesses one electron more than SF_6 and one valence electron less than XeF_6 so that the unpaired electron is expected to occupy the a^*_{1g} orbital in O_h symmetry. Since the a^*_{1g} orbital is thought to play a pivotal role in the unusual structural dynamics of XeF_6 ,²⁻⁴ it is of interest to ascertain the composition of this antibonding orbital in related radicals by ESR studies. We now wish to report the preparation and ESR identification of the ClF_6 radical.

The title radical was generated by γ radiolysis of SF_6 containing 5 mol % of ClF_3 at -196° . Fessenden and Schuler⁵ have described the use of solid SF_6 as a suitable matrix for the observation of isotropic ESR spectra during in situ irradiation.⁶ Similarly, we find that isotropic spectra are observed for radicals which are sufficiently long-lived to be detected in a γ -irradiated SF_6 matrix at -165° .

In the spectrum shown in Figure 1, the outer lines consist predominantly of two separate 1:6:15:20:15:6:1 septets at low field together with a corresponding septet at high field. Allowing for the effect of radical decay during the sweep from low to high field, these three septets are of comparable intensity. Accordingly, the pattern is interpreted as a 1:1:1:1 quartet of binomial septets, the missing septet being masked by the more intense lines from SF_5^{\cdot} and ClF_4^{\cdot} in the center of the spectrum. The septet substructure is attributed to hyperfine interaction with six equivalent fluorine ($I = 1/2$) nuclei while the quartet splitting originates from coupling to one ^{35}Cl ($I = 3/2$) nucleus.⁹ This interpretation is verified by the observation of the outer components from the weaker spectrum of the ^{37}Cl ($I = 3/2$) radical, as indicated in Figure 1.

Because of the large hyperfine interactions, the ESR parameters were calculated by including terms up to fourth order in the solution of the isotropic ESR spin Hamilto-

nian.¹⁰ These values were then refined until forward calculations by means of an accurate expression¹¹ derived from the Breit-Rabi equation reproduced the experimental field positions of the outer ($M_I(\text{Cl}) = \pm 3/2$) components, the following results being obtained: $a(^{35}\text{Cl}) = 771$ G, $a(^{37}\text{Cl}) = 642$ G, $a(^{19}\text{F}) = 89$ G, and $g = 2.015 \pm 0.001$. It is estimated that the hyperfine coupling constants are accurate to ± 1 G. The ratio of $a(^{35}\text{Cl})/a(^{37}\text{Cl})$ is 1.201 ± 0.002 , in satisfactory agreement with the value of 1.2015 for the $^{35}\text{Cl}/^{37}\text{Cl}$ ratio of nuclear g factors. An additional check on the parameters was made by calculating the field positions for the $M_I(^{35}\text{Cl}) = +1/2$ set of components, these values agreeing with the observed positions to better than 1 G.

The spectrum of interest is assigned to the ClF_6 radical formed by fluorine atom addition or transfer to ClF_5 . The most remarkable feature is the large ^{35}Cl coupling of 771 G which is more than twice the value (288 G) for ClF_3 .⁸ Since an isotropic coupling of only 82 G has been calculated for complete occupancy of the chlorine 4s orbital,^{8a} it is evident that the unpaired electron in ClF_6 must populate the chlorine 3s orbital. In this case the coupling corresponds to a spin density of 0.46. This finding is consistent with the occupation of the totally symmetric a^*_{1g} orbital for a regular octahedral geometry. Also, the interaction with six equivalent fluorines accords with this description.

Although the results conform to O_h symmetry, they do not eliminate the possibility that ClF_6 undergoes deformations similar to those deduced for XeF_6 .^{2a} First, such motions would lead to such a rapid modulation of the spin distribution that the fluorines would be equivalent on the ESR time scale. Secondly, the results of Hückel MO calculations indicate that the HOMO of XeF_6 is stabilized by deformations from O_h to C_{3v} symmetry when there is a large contribution from the xenon 5s orbital to this antibonding orbital.^{2b} Therefore the large spin density in the chlorine 3s orbital of ClF_6 is quite compatible with a fluctuating structure involving deformations to nonoctahedral configurations.

Finally, it is noteworthy that the lines of the ClF_6 spec-

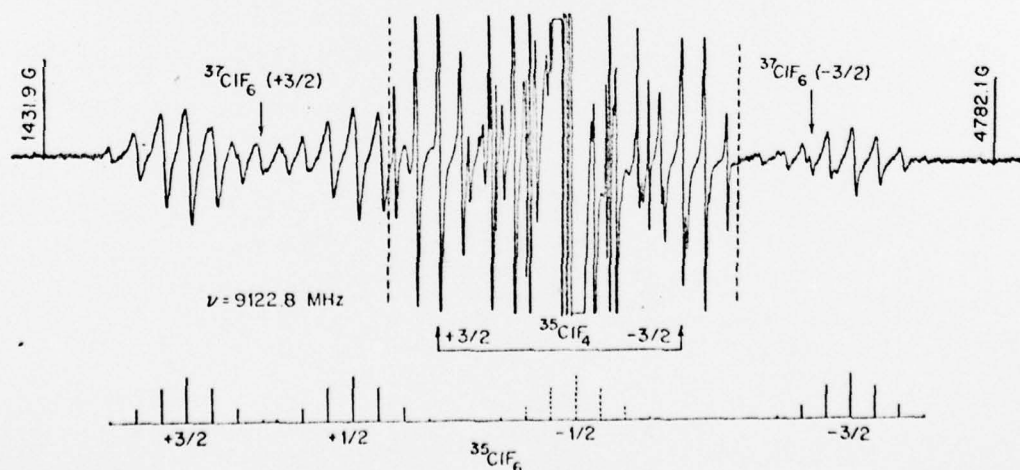


Figure 1. First-derivative ESR spectrum of γ -irradiated SF_6 containing ClF_3 at -165° . The center portion of the spectrum was recorded at approximately half the gain in order to show the outer quintets of the ClF_4 spectrum; strong lines from SF_5^{\cdot} are also present in the center region. The line positions for the $^{35}\text{ClF}_6$ spectrum are indicated by the stick diagram and the arrows above the spectrum mark the center lines of the outer septets of $^{37}\text{ClF}_6$.

trum are much broader than those of the ClF_4 spectrum in Figure 1. The broadening appears to be uniform for the different components and therefore is not attributable to a modulation of the spin distribution (on the ESR time scale) nor to anisotropic broadening resulting from incomplete tumbling of the ClF_6 radical. It is conceivable that the broadening is caused by enhanced spin-lattice relaxation through a mechanism of spin-orbit coupling.¹² Such a mechanism might well be operative if there is a mixing of the $(a^*_{1g})^1$ ground state configuration with the orbitally degenerate $(a^*_{1g})^0 (t^*_{1u})^1$ excited state during the course of deformations about a mean of octahedral geometry. A pseudo-Jahn-Teller effect of this type has been discussed^{2a} in the analogous case of XeF_6 .

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References and Notes

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- (8) (a) J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 3112 (1973). (b) Also, an intense ESR spectrum of ClF_4 was observed after γ irradiation of SF_6 containing chlorine trifluoride. This method of generation differs from that used by Morton and Preston^{7a} and thereby confirms their identification of the ClF_4 radical.
- (9) The absence of a central septet spectrum with 500-fold greater intensity rules out the possibility that the quartet of septets is due to ^{23}S ($I = \frac{3}{2}$) satellites in natural abundance. Also, the spectrum reported in this paper is clearly different from a weak spectrum noted previously⁹ for a radical with six equivalent fluorines and thought to be SF_6^+ . The latter spectrum ($a(^{19}\text{F}) = 195 \text{ G}$; $g = 2.006$) possessing well-resolved second-order fluorine splittings has been also observed in our studies of γ -irradiated SF_6 without additives.
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ESR spectrum and structure of BrF_6^* Koichi Nishikida, Firancon Williams,[†] Gleb Mamantov, and Norman SmyrlDepartment of Chemistry, University of Tennessee, Knoxville, Tennessee 37916
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Recently, we reported the isotropic ESR spectrum of the ClF_6 radical¹ showing equal hyperfine interaction with six fluorines ($a_{19} = 89$ G) and an extremely large chlorine coupling ($a_{35} = 771$ G) corresponding to a spin density of 0.48 in the $3s$ orbital of the central atom. We now describe similar studies designed to prepare and detect the heavier congeneric radicals BrF_6 and IF_6 .

A gaseous mixture consisting of ~5 mole% of the halogen pentafluoride in SF_6 was made up in a well-passivated metal vacuum line and condensed directly into a Suprasil quartz tube. The resulting solid solution was γ irradiated at 77 °K and the X-band ESR spectra recorded at ~105 °K, the technique being adapted from that originally employed by Fessenden and Schuler.² The magnetic field strengths in the electron resonance region were determined using a proton magnetic resonance probe. Except for the well-known signals of the radicals derived from the SF_6 host,³⁻⁵ no isotropic ESR transitions were detected in the iodine pentafluoride sample by sweeping the magnetic field from zero to 13 kG.

As shown in Fig. 1, a group of evenly spaced transitions were observed between 6.5 and 7.5 kG in the BrF_5 mixture. Assuming that $g \sim 2$, the abbreviated form of the spectrum is indicative¹ of a large bromine hyperfine interaction such that only the lines belonging to the high-field quantum number $M_I = -3/2$ transitions of a bromine ($I = 3/2$ for ^{79}Br and ^{81}Br) radical are observed, the substructure representing the additional coupling to several equivalent fluorines. A clue to the identity of the radical is provided by the uniform 90 ± 1 G spacing between the broad lines, this value being almost identical to the fluorine coupling (89 G) in the ClF_6 radical.¹ In addition, the nonbinomial intensity distribution for the seven strong components is accounted for if the spectrum represents a superimposition of hyperfine components from ^{79}Br and ^{81}Br species present in almost equal abundance. As shown in the stick diagram, a satisfactory reconstruction of the nine-line spectrum is obtained by positioning the two 1:6:15:20:15:6:1 fluorine septets from $^{79}\text{BrF}_6$ and $^{81}\text{BrF}_6$ so that their center lines are

separated by twice the fluorine splitting.

In order to obtain the bromine hyperfine couplings, the exact (Breit-Rabi) solution⁶ of the isotropic spin Hamiltonian for $S = \frac{1}{2}$ and $I = \frac{3}{2}$ was used to construct an energy-level diagram.⁶ Because the bromine hyperfine interaction is comparable to the electron Zeeman energy, the two spin angular momentum vector S and I are coupled to form a resultant $F = S + I$ and the eigenstates are specified by the $|F, M_F\rangle$ quantum numbers where F is the total angular momentum and M_F is its z component. Thus, there are two levels $F = 2$ and $F = 1$, each consisting of $2F + 1$ sublevels in a magnetic field with different values of $M_F = M_S + M_I$.

When the zero-field splitting $(I + 1/2)a = 2a$ (in MHz) exceeds the microwave frequency ν , the only transition allowed in the high-field limit ($\Delta M_I = 0$) is that between

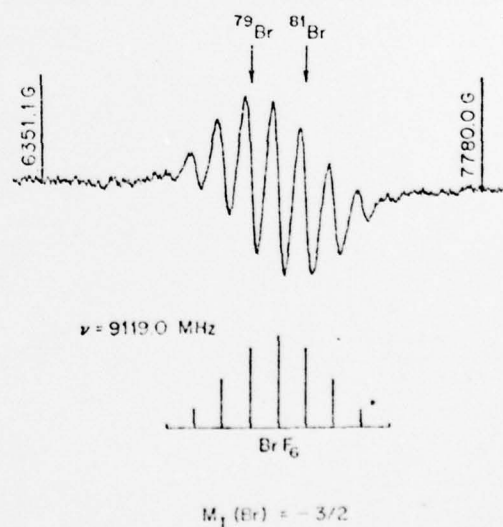


FIG. 1. ESR spectrum of BrF_6 showing the $12, -2) \leftrightarrow 12, -1)$ bromine transitions with fluorine substructure.

TABLE I. ESR transitions and hyperfine interaction parameters for BrF_6 .

ν MHz	$H_{-3/2} (^{81}\text{Br})$ G	$H_{-3/2} (^{79}\text{Br})$ G	a_{31}^a MHz	a_{79}^a MHz	a_{19}^b MHz
9121.1	7211.1	7032.4	12 670	11 735	252
9118.8	7211.3	7032.9	12 678	11 744	252

^aCalculated using Eq. (2) and $g=2.015$; values obtained using Eq. (1) differed from these by ~ 6 MHz which is within the precision of the results.

^bFluorine coupling obtained directly from spectrum (see Fig. 1 and text).

the $|2, -2\rangle$ and $|2, -1\rangle$ states corresponding to $M_I = -\frac{3}{2}$.⁷ It is easily shown that the magnetic field at resonance $H_{-3/2}$ is given exactly by Eq. (1),

$$\frac{g\beta H_{-3/2}}{h} \left\{ 2\nu' + a \left(1 - \frac{g_N \beta_N}{g\beta} \right) + \frac{g_N \beta_N H_{-3/2}}{h} \left(1 + \frac{g_N \beta_N}{2g\beta} \right) \right\} = 2\nu'(\nu' + 2a), \quad (1)$$

where $\nu' = \nu + g_N \beta_N H_{-3/2}/2h$ and the other symbols have their usual connotations. Assuming that the nuclear Zeeman term $g_N \beta_N H_{-3/2}/h$ is negligible compared to ν , a , and $g\beta H_{-3/2}/h$, Eq. (1) reduces to

$$\frac{g\beta H_{-3/2}}{h} = 2\nu' \left(\frac{\nu + 2a}{2\nu + a} \right), \quad (2)$$

which allows a to be evaluated directly from a knowledge of $H_{-3/2}$, ν , and g . Since there is no spectrum from bromine isotopes with zero spin, the g factor of BrF_6 cannot be determined independently and we have assumed the value obtained for ClF_6 ,¹ viz., 2.015.

The coupling constants derived from two sets of experimental data are given in Table I, the average values being $a_{81} = 4494 \pm 2$ G, $a_{79} = 4163 \pm 2$ G, and $a_{19} = 89 \pm 1$ G. The ratio a_{81}/a_{79} is 1.079 in satisfactory agreement with $\mu_{81}/\mu_{79} = 1.078$, thereby confirming the above analysis

and the assignment of the spectrum to BrF_6 . Employing the magnetic parameters calculated for the bromine 4s atomic orbital,⁸ these bromine coupling constants correspond to a 4s spin density of 0.54 on the central atom which compares closely with the value of 0.46 obtained for the chlorine 3s orbital in ClF_6 .¹ Thus the distribution of the unpaired electron between the ns orbital of the central atom and the fluorine ligands is very similar in the two radicals and these results are consistent with the occupation of the totally symmetric a_{1g}^* orbital in O_h symmetry. However, as mentioned previously,¹ these results do not exclude the possibility of large deformations about a mean of octahedral geometry, and the large ESR linewidths may be symptomatic of a fluctuating structure.

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⁶See, e.g., G. E. Pike and T. L. Estle, *The Physical Principles of Electron Paramagnetic Resonance* (Benjamin, Reading, MA, 1973), 2nd ed., p. 117.

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